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TITLE: POLYLACTIC ACID RESIN FOAM AND METHOD FOR PRODUCING THE SAME

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ABSTRACT:

PROBLEM TO BE SOLVED: To provide a good-quality polylactic acid resin foam having a uniform and fine foam, particularly a foam of high magnification and high closed cell ratio by the extrusion foaming of the polylactic acid resin.

SOLUTION: The extrusion foaming is carried out by selecting and using the amorphous polylactic acid resin having a melt viscosity ranging from 1.0×10⁸ to 3.0×10⁶ PaS at 75°C and ranging from 1.0×10⁶ to 3.0×10⁵ PaS at 100°C, and by using a hydrocarbon and carbon dioxide as foaming agents.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to polylactic acid system resin foam and its manufacture approach.

[0002]

[Description of the Prior Art] Polylactic acid system resin is known as resin which is easy to biodegrade. That is, it is said that it will be automatically decomposed during a little less than one year, and polylactic acid system resin will mainly become water and a harmless thing like a carbon dioxide if this is buried underground. For this reason, polylactic acid system resin has come to be recently brought into the limelight suddenly as resin which serves as dust forever like conventional plastics, and does not remain, therefore does not pollute an environment.

[0003] Although a lactic acid may mean a beta-hydroxy propionic acid rarely, an alpha hydroxypropionic acid shall usually be pointed out to it. Since the alpha hydroxypropionic acid contains the asymmetric carbon atom in the molecule, optical activity is shown, therefore three sorts of things, D-object, L-object, and racemic modification (D, L-object), exist in this acid. Therefore, the polylactic acid which was made to carry out the polymerization of this acid, and was obtained becomes the mixed rate of these three sorts of things, and the thing from which the property differed [that it is various and] according to the difference of a polymerization method etc. In fact, there are various things from which the property differed greatly from the crystalline thing to the thing of amorphism nature in polylactic acid.

[0004] Commercially, polylactic acid is still in a prototype phase, and cannot come to hand easily in a commercial scene. At present, although it can obtain as a sample, if the physical properties of the sample are not clarified in many cases and result in the manufacture approach, they are in the condition which is not known at all.

[0005] Since the tension of polylactic acid at the time of melting is low, it is supposed that it is resin which is hard to make it foam. Therefore, there is little what has indicated this about the foaming approach of polylactic acid. It has proposed that JP,2000-7815,A adds a thickener to polylactic acid, extrudes this, makes it foam, and considers as foam in order to carry out that it is easy to make polylactic acid foam. Although it is explaining that this official report can use organic compounds various as a thickener, in the example, an inorganic substance like a boric acid is only used, and it does not explain at all what kind of melt viscosity it should make. Moreover, although it is explaining that this official report can use organic compounds various as a foaming agent, the carbon dioxide is used in the example. In addition, although the example has indicated that it was able to be made to foam 17 to 22 times, in having used the above-mentioned thing for the thickener and the foaming agent, it is very difficult to make it foam to about 20 times.

[0006] Moreover, in order to carry out that it is easy to make polylactic acid foam, JP,2000-7816,A added the inorganic filler and the foaming assistant to polylactic acid, and has proposed carrying out extrusion foaming. Although it is explained as an inorganic filler that various things, such as a silica and

a zeolite, can be used, it is explained that metallic soap like calcium stearate as a foaming assistant can be used and it is explained that still more nearly various organic substance as a foaming agent can be used, in the example, the carbon dioxide is used as calcium stearate or montanoic acid calcium, and a foaming agent as talc and a foaming assistant as an inorganic filler. Therefore, the foam obtained in the example remains in the low thing of 5.8 to 6.4 times in expansion ratio.

[0007]

[Problem(s) to be Solved by the Invention] It was difficult to have made polylactic acid foam for a high scale factor easily as mentioned above in a conventional method. Then, this invention tends to offer the approach of obtaining easily and certainly the good polylactic acid foam to which it foamed uniformly minutely and especially the rate of a closed cell foamed for the high scale factor highly by improving the fault of the above conventional techniques, extruding polylactic acid and making it foam.

[0008]

[Means for Solving the Problem] In order to solve an above-mentioned technical problem, this artificer put various polylactic acid into the extruder, pressed foaming agents various within an extruder fit, extruded under various extrusion conditions, foamed, and considered synthetically the relation between a foaming agent and extrusion conditions. Consequently, in order to make polylactic acid foam for a high scale factor certainly and easily, maintaining the melt viscosity of polylactic acid, as it is in a certain within the limits has noticed it being more important than anything.

[0009] The manufacturer of polylactic acid exhibits physical properties slightly about the polylactic acid which self manufactured. The physical properties currently exhibited have distinction of whether polylactic acid is the thing of whether it is a crystalline thing and amorphism nature, and the main numeric value of mechanical physical properties, such as tensile strength, and flexural strength, a consistency, and it is not officially announced at all about the thermal property especially the melting point, or melt viscosity of polylactic acid. Therefore, this artificer measured melt viscosity about the product of each company. Consequently, since crystalline polylactic acid is rapidly fused near the crystalline melting point compared with the polylactic acid of amorphism nature and reduced viscosity, it found out that it was not suitable for carrying out extrusion foaming.

[0010] Then, the melting property was further examined about the polylactic acid of amorphism nature. Consequently, the polylactic acid of amorphism nature found out that the melt viscosity between about 75 degrees C and 100 degrees C was important, in order to extrude the polylactic acid of amorphism nature and to have made it foam, since it was while the glass transition point was about 50-65 degrees C.

[0011] Then, the cupping test was performed about further various kinds of amorphous polylactic acid, temperature of polylactic acid was made into at least 75 degrees C and a maximum of 100 degrees C, the melt viscosity of the polylactic acid in the intermediate temperature was measured, and it strove for specification of the melt viscosity of the polylactic acid suitable for foaming. Consequently, polylactic acid found out that extrusion foaming became easy, when the related curve of the melt viscosity and temperature was within the limits of specification.

[0012] Here, specific relation is the relation that a melt viscosity curve must exist in a shadow area A in drawing 1, when the temperature expressed with the axis of abscissa by Centigrade is taken, the melt viscosity of the polylactic acid which expressed with a pascal and a second (PaS) to the axis of ordinate is taken and a melt viscosity curve is made. What a shadow area A has melt viscosity within the limits of 1.0×10^8 PaS to 3.0×10^6 PaS in 75 degrees C, and is within the limits of 1.0×10^6 PaS to 3.0×10^5 PaS in 100 degrees C is shown.

[0013] Moreover, since the viscosity of polylactic acid fell with lifting of temperature, when it usually specified the melt viscosity in 75 degrees C and 100 degrees C as mentioned above, the melt viscosity in the intermediate temperature between 75 degrees C and 100 degrees C checked existing between the line which connects the peak price of ends temperature, and the line which connects the minimum value.

[0014] Moreover, above-mentioned relation is being able to say also about the copolymer of polylactic acid and a lactic acid. Here, the copolymer of a lactic acid has pointed out the copolymer of a lactic acid and aliphatic series hydroxycarboxylic acid other than a lactic acid.

[0015] By the way, there is almost that [no] by which the melt viscosity enters in the shadow area A of drawing 1 in the sample of polylactic acid at present. Almost all samples have viscosity far higher than what enters in a shadow area A. This is clear by JP,2000-7815,A and the 2000 No. -7816 official report. It is because a cylinder temperature is made into 170 to 180 degree C, it holds in the example of these official reports to high temperature which calls T-die temperature 140 degrees C and extrusion foaming is performed.

[0016] Therefore, this invention choosing and using the polylactic acid system resin with a melt viscosity curve of amorphism nature into the shadow area A shown in drawing 1, and extruding this and making it foaming is not made until now.

[0017] Furthermore, this artificer found out that the good foam which foamed for the high scale factor with the high rate of a closed cell could be obtained easily and certainly rather than the case where other foaming agents are used when extruding polylactic acid system resin with the melt viscosity curve which enters in a shadow area A as mentioned above, making it foam, the mixture of the hydrocarbon and carbon dioxide like butane as a foaming agent was used and each is used independently. This invention is completed based on such knowledge.

[0018] this invention -- melt viscosity -- 75 degrees C -- setting -- 1.0x108 from -- within the limits of 3.0x106PaS -- it is -- 100 degrees C -- setting -- 1.0x106 from -- the polylactic acid system resin of the amorphism nature which is within the limits of 3.0x105PaS is fused within an extruder, a hydrocarbon and a carbon dioxide are pressed fit in this as a foaming agent, and the manufacture approach of the polylactic acid system resin foam characterized by performing extrusion foaming is offered.

[0019] Since polylactic acid system resin is resin which is hard to make it foam as mentioned above, it is difficult to make this resin foam to homogeneity, furthermore it is much more difficult to make this resin foam so that air bubbles may become detailed. However, the polylactic acid system resin foam obtained by this invention approach Have the air bubbles to which within the limits of 0.1-0.5mm was equal, and it follows. homogeneity -- it is not only good foam to which it foamed minutely -- further -- a high scale factor -- foaming -- 30 - 90 kg/m³ It should have the low consistency which is said. ** -- Moreover, this artificer found out that especially the rate of a closed cell was the high thing which it especially says is 85% or more 50% or more.

[0020] therefore, this invention -- melt viscosity -- 75 degrees C -- setting -- 1.0x108 from -- within the limits of 3.0x106 PaS -- it is -- 100 degrees C -- setting -- 1.0x106 from -- the homogeneity which extrude the polylactic acid system resin of the amorphism nature which is within the limits of 3.0x105 PaS, it was made to foam, and was acquired -- the polylactic acid system resin foam to which it foamed minutely is offered. Furthermore, this invention foams for a high scale factor also among the above-mentioned foam, and a consistency is 30 - 90 kg/m³. It is the low value which is said and the unique foam in which the rate of a closed cell moreover had a high value of 50% or more is offered.

[0021] By this invention approach, melt viscosity was measured by the following approaches. The melting extension floating measuring device (Oriental energy machine company make, mel ten rheometer) was used for measurement. Moreover, what was fabricated to the cylindrical shape with a diameter [of 8.5mm] and a height of 180mm was used for the test sample. After checking that the sample was immersed in the oil bath (75 degrees C and 100 degrees C) for 10 minutes, and the whole sample has become the temperature of homogeneity, they are rate of strain 0.1S-1 It carried out and extension viscosity 1 second after beginning to pull was made into melt viscosity. Moreover, the diameter of air bubbles was measured based on ASTMD-2842-69.

[0022] In this invention, polylactic acid system resin of amorphism nature with which the melt viscosity curve of resin enters in the shadow area A of drawing 1 is chosen and used, and it is important to press a hydrocarbon and a carbon dioxide fit in the resin fused within the extruder, and it is extruded and performs [the rest keeps desirable 75-100 degrees C of resin temperature at the time within the limits of 80-95 degrees C, and] extrusion foaming. In addition, in order to carry out that it is easy to make it foam, it is the same as knockout foaming of conventional resin that various foaming nucleating additives and foaming assistants may be added.

[0023] By this invention, the mixture of a hydrocarbon and a carbon dioxide is used as a foaming agent

because the foam it being not only easy to make polylactic acid system resin foam uniformly minutely but obtained when that mixture was used becomes what foamed for the high scale factor with the high rate of a closed cell and reinforcement becomes an adiathermic good large thing. As a hydrocarbon, it is suitable to use aliphatic hydrocarbon, such as ethane, a propane, butane, a pentane, a hexane, ethylene, a propylene, and the petroleum ether. Although it has the capacity in which polylactic acid system resin is made to foam even when these hydrocarbons are independent, the foam obtained by the independent activity of a hydrocarbon has the permeability which becomes what has a low rate of a closed cell, therefore air bubbles opened for free passage mutually. For this reason, the obtained foam becomes the weak thing of a mechanical strength which has low heat insulation. However, if a hydrocarbon and a carbon dioxide are used as a foaming agent, the rate of a closed cell will be high, the obtained foam will be rich in adiathermic, and it will become what has large reinforcement.

[0024] Although above-mentioned ethane, the propane of the hydrocarbon used as a foaming agent by this invention, etc. may be independent, they may be mixture, such as ethane and a propane. Especially among hydrocarbons, butane is desirable. In addition, in this invention, what carried out little addition of halogenated aliphatic hydrocarbon, nitrogen, etc., such as a methyl chloride and an ethyl chloride, further can be used for a hydrocarbon and a carbon dioxide as a foaming agent.

[0025] Moreover, it is desirable that the rates of a hydrocarbon and a carbon dioxide of occupying are 90 - 50 % of the weight and 10 - 50 % of the weight in a foaming agent in this case, respectively. Still more desirable rates are 90 - 70 % of the weight, and 10 - 30 % of the weight. The reason is that a cavity will stop generating to the foam which it prevented foaming within metal mold with a carbon dioxide, and it not only becomes it is few and easy to foam contraction of the resin after extrusion foaming, but was obtained, and the rate of a closed cell will become high, therefore foam will become heat insulation and the thing whose mechanical strength improved if the foaming agent contains the hydrocarbon and the carbon dioxide at such a rate.

[0026] As a foaming nucleating additive, the fines of an inorganic [well-known] or an organic substance which serves as a nucleus of foaming can be added. As an inorganic substance, talc, a silica, etc. can be used, for example. Moreover, it can be made to foam smoothly by added and extruding metallic soap, such as calcium stearate, as a foaming assistant. In addition, a coloring agent, an antioxidant, etc. can also be added according to the object.

[0027]

[Effect of the Invention] Since the polylactic acid system resin with melt viscosity which has a melt viscosity curve in the shadow area A of drawing 1 of amorphism nature is used according to this invention approach if it resays -- melt viscosity -- 75 degrees C -- setting -- 1.0x10⁸ from -- within the limits of 3.0x10⁶ PaS -- it is -- 100 degrees C -- setting -- 1.0x10⁶ from, since the resin which is within the limits of 3.0x10⁵ PaS is used When this is extruded and is made to foam at the temperature of 80-95 degrees C preferably 75-100 degrees C within an extruder, polylactic acid system resin will have the melt viscosity suitable for foaming. Therefore, according to this invention approach, the good polylactic acid system resin foam which foamed for the high scale factor can be obtained easily and certainly. Moreover, the foam from which it extruded since the mixture of a hydrocarbon and a carbon dioxide was used as a foaming agent, and foaming not only becomes easy, but was obtained foams uniformly minutely, and it becomes what has a large rate of a closed cell, therefore heat insulation becomes the good large thing of a mechanical strength. At this point, this invention approach gives a big profit.

[0028] It is the description to foam uniformly [the polylactic acid system resin foam obtained by this invention] minutely. It has the air bubbles to which within the limits whose diameter of average air bubbles is 0.1-0.5mm as foaming uniformly minutely was equal. It is especially desirable that it is a thing within the limits of 0.15-0.25mm. moreover, this foam -- a consistency -- 30 - 90 kg/m³ -- especially -- 40 - 60 kg/m³ ** -- it becomes what gathered uniformly by the low consistency to say, and the rate of a closed cell becomes 85% or more of especially high thing 50% or more. Therefore, especially as for this foam, 0.03 or less W/mk of thermal conductivity becomes the low thing of 0.027 or less W/mk. And this foam is obtained as a big thing several 10mm and whose width of face thickness is hundreds of mm. Therefore, this foam can be used for various applications.

[0029] An example and the example of a comparison are given to below, and the detail of this invention approach is explained. In addition, it is ASTM so that these measurement may be described below, although the rate of a closed cell and the rate of an open cell were measured about the obtained foam in the example and the example of a comparison. It carries out based on D-2856-70. That is, except for the epidermis part of foam, five test pieces which cut foam on 25mm square were prepared first. As a measuring device, the air relation aerometer 1000 mold (the Tokyo Saiensu-Sha make) was used. Subsequently, based on ASTMD-2856-70, the rate of a closed cell and the rate of an open cell of a test piece were measured, and the acquired value was averaged and it considered as each value.

[0030] Moreover, it is JIS although thermal conductivity was measured. A It measured based on 1412. That is, what passed for two months from the manufacture date of foam was cut in the thickness of 25mm, die length of 200mm, and width of face of 200mm, it considered as the test piece, the heat flow which passes this test piece was measured with the plate heat flux meter of two sheets, and the temperature gradient of the test piece at that time was measured. The obtained heat flow and the value calculated from the temperature gradient were made into thermal conductivity.

[0031]

[Example 1] As resin, the melt viscosity in 75 degrees C is 1.0×10^7 PaS, and the polylactic acid of amorphism nature adjusted so that the melt viscosity in 100 degrees C might be 6.0×10^5 PaS was used. The glass transition point of this resin was 53 degrees C. The mixture which added the high DOROSE roll CF(product made from BERINGA) 0.3 weight section to this resin 100 weight section, and was obtained was supplied to the tandem extruder (50 to 60 mm aperture). While carrying out melting kneading of the resin within the 1st extruder, as a foaming agent, butane is the 5.0 weight sections and a carbon dioxide is the 1.0 weight section. 83.3% of the weight, the rate that the butane in a foaming agent occupies presses fit that from which the rate that the carbon dioxide in a foaming agent occupies is 16.7 % of the weight, and cools resin temperature for this to 84 degrees C within delivery and the 2nd extruder to the 2nd extruder. It was made to extrude and foam from a mouthpiece with a slit 2mm and a width of face of 90mm to the bottom of pressure 12MPa.

[0032] The diameter of air bubbles foamed to the obtained foam uniformly minutely by the average of about 0.20mm, and it was a good thing whose consistencies are 41.2 kg/m³, the thickness of 28mm, and width of face of 215mm. Moreover, the rate of an open cell is low, this foam was 6.4%, and the rate of a closed cell was 90.5%. Moreover, thermal conductivity was 0.0262 W/mk.

[0033]

[Example 2] As resin, the melt viscosity in 75 degrees C is 1.0×10^7 PaS, and the melt viscosity in 100 degrees C used the amorphous polylactic acid which is 6.0×10^5 PaS. The glass transition point of this resin was 53 degrees C. It carried out completely like [this resin 100 section] the example 1 except the rate that the butane in a foaming agent occupies [butane / the 3.8 weight sections and a carbon dioxide] in 2 weight sections having decided to press fit that from which the rate that the carbon dioxide in a foaming agent occupies 65.5% of the weight is 34.5 % of the weight, and to extrude with the resin temperature of 87 degrees C, extruded, and was made to foam.

[0034] The diameter of air bubbles foamed to the obtained foam uniformly minutely by an average of 0.18mm, and it was a good thing whose consistencies are 44.3 kg/m³, the thickness of 27mm, and width of face of 220mm. Moreover, the rate of an open cell of this foam was 5.9%, and the rate of a closed cell was 91.2%. Moreover, thermal conductivity was 0.0258 W/mk.

[0035]

[Example 3] As resin, the melt viscosity in 75 degrees C is 1.0×10^7 PaS, and the melt viscosity in 100 degrees C used the amorphous polylactic acid which is 6.0×10^5 PaS. The glass transition point of this resin was 53 degrees C. Butane made this resin 100 section carry out extrusion foaming completely like an example 1 except the rate that the butane in a foaming agent occupies [the 3.0 weight sections and a carbon dioxide] in the 2.5 weight sections having decided to press fit that from which the rate that the carbon dioxide in a foaming agent occupies is 45.5 % of the weight 54.5% of the weight, and to extrude this at 90 degrees C.

[0036] The diameter of air bubbles was foaming to the obtained foam uniformly minutely by 0.15mm,

and it was a good thing whose consistencies are 47.1 kg/m³, the thickness of 26mm, and width of face of 222mm. Moreover, the rate of an open cell of this foam was 5.5%, the rate of a closed cell was 91.5%, and thermal conductivity was 0.0255 W/mk.

[0037]

[Example 4] As resin, the melt viscosity in 75 degrees C is 3.0x10⁷ PaS, and the melt viscosity in 100 degrees C used the amorphous polylactic acid which is 9.0x10⁵ PaS. The glass transition point of this resin was 54 degrees C. Butane made this resin 100 weight section carry out extrusion foaming completely like an example 1 except the rate that the butane in a foaming agent occupies [the 5.0 weight sections and a carbon dioxide] in the 1.0 weight section having decided to press fit that from which the rate that the carbon dioxide in a foaming agent occupies is 16.7 % of the weight 83.3% of the weight, and to extrude this at 90 degrees C.

[0038] The diameter of air bubbles was foaming to the obtained foam uniformly minutely by 0.23mm, and it was a good thing whose consistencies are 44.0 kg/m³, the thickness of 28mm, and width of face of 214mm. Moreover, the rate of an open cell of this foam was 6.7%, the rate of a closed cell was 89.9%, and thermal conductivity was 0.0265 W/mk.

[0039]

[The example 1 of a comparison] As resin, the melt viscosity in 75 degrees C is 7.0x10⁸ PaS, and the melt viscosity in 100 degrees C used the amorphous polylactic acid which is 2.0x10⁶ PaS. The glass transition point of this resin was 55 degrees C. The butane 6.5 weight section is pressed fit in this resin 100 weight section, and it extruded completely like the example 1 and was made to foam except having decided to make resin temperature into 78 degrees C, and to extrude it.

[0040] By this approach, it contracted, after the extruded resin foaming, and the consistency became 122 kg/m³, and very heavy good foam was not obtained.

[0041]

[The example 2 of a comparison] As resin, the melt viscosity in 75 degrees C is 3.0x10⁷ PaS, and the melt viscosity in 100 degrees C used the amorphous polylactic acid which is 9.0x10⁵ PaS. The glass transition point of this resin was 53 degrees C. The carbon-dioxide 4.5 weight section is pressed fit in this resin 100 weight section, and it extruded completely like the example 1 and was made to foam except having decided to make resin temperature into 98 degrees C, and to extrude it.

[0042] The cavity occurred inside and the obtained foam did not turn into good foam.

[0043]

[The example 3 of a comparison] As resin, the melt viscosity in 75 degrees C is 7.0x10⁸ PaS, and the melt viscosity in 100 degrees C used the amorphous polylactic acid of 2.0x10⁶ PaS. The glass transition point of this resin was 53 degrees C. It extruded completely like the example 1 and was made to foam except having carried out 1.0 weight section press fit of the 5.0 weight sections and the carbon dioxide for butane at this resin 100 weight section, and having decided to make resin temperature into 101 degrees C, and to extrude it.

[0044] The obtained foam did not have a fixed configuration, and variation was large and a consistency's was not good.

[0045]

[The example 4 of a comparison] As resin, the melt viscosity in 75 degrees C is 8.0x10⁵ PaS, and the melt viscosity in 100 degrees C used the amorphous polylactic acid of 1.0x10⁵ PaS. The glass transition point of this resin was 53 degrees C. The 1.0 weight section is pressed fit in this resin 100 weight section for the butane 5.0 weight section and a carbon dioxide, and it extruded completely like the example 1 and was made to foam except having decided to make resin temperature into 78 degrees C, and to extrude it.

[0046] The obtained foam did not have a fixed configuration, and variation was large and a consistency's was not good.

[Translation done.]